FLAME AND SHRINKAGE RESISTANT FABRIC BLENDS

CROSS-REFERENCE TO RELATED APPLICATION

This is a continuation of U.S. Patent Application Serial No. 09/657,047, filed August 28, 2000, entitled "Flame and Shrinkage Resistant Fabric Blends," which is a continuation-in-part application of U.S. Patent Application Serial No. 09/062,805, filed April 20, 1998, entitled "Flame and Shrinkage Resistant Fabric Blends and Method for Making Same" (now U.S. Patent No. 6,132,476).

FIELD OF THE INVENTION

The present invention relates to flame resistant fabrics. More particularly, the present invention relates to fabric blends containing inherently flame resistant fibers and flame resistant cellulosic fibers that contain a flame retardant compound. These fabrics exhibit excellent flame resistance, minimal shrinkage when laundered, and can be produced in a full range of colors and shades.

BACKGROUND OF THE INVENTION

Inherently flame resistant fibers are highly resistant to heat decomposition and are therefore desirable in the manufacture of flame resistant garments intended for environments in which flames or extreme heat will be encountered. These desirable

properties of inherently flame resistant fibers can, however, create difficulties during fabric production. For example, fibers composed of aromatic polyamide, commonly known as aramid fibers, are difficult to dye. Aramid fiber suppliers have recommended complicated exhaust dyeing procedures with various dye-assistants, high temperatures, and long dyeing times to effect dyeing of these fibers. Such dyeing conditions require substantial amounts of energy both to maintain the dyeing temperature and for the treatment of waste dyebaths. Dye-assistants comprised of organic agents, and commonly referred to as carriers or swelling agents, are used to enhance dyeability. Such dye-assistants may be added to the dyebath as a treatment prior to dyeing, or can be integrated into the inherently flame resistant fiber during its production.

Inherently flame resistant fibers such as aramid fibers can be blended with fibers made of other materials. As is known in the art, fiber blending can be used to obtain an end fabric that combines the beneficial characteristics of each of the constituent fibers. For instance, in the area of flame resistant fabric manufacture, flame resistant cellulosic fibers such as flame resistant rayon ("FR rayon") fibers can be successfully blended with aramid fibers to obtain a flame resistant material which is softer, more moisture absorbent, and less expensive to produce than materials constructed only of aramid fibers.

Although improving the texture and lowering the cost of flame resistant fabrics, blending inherently flame resistant fibers with flame resistant cellulosics such as FR rayon can complicate production. Specifically, cellulosics contain flame retardant agents that, although resistant to standard cellulosic dyeing procedures, tend to be depleted by the extreme temperatures generally considered necessary to dye the inherently flame resistant fibers. This depletion of flame retardant agents significantly reduces the flame

resistance of the cellulosic fibers and therefore reduces the flame resistance of these blends. Moreover, these conditions increase the likelihood of further depletion of the flame retardant agents during subsequent launderings and an even greater reduction in flame resistance.

Due to the danger of depleting the flame retardant agent or agents contained in the cellulosic fibers of such fabric blends, producers of cellulosic fibers often advise their customers to avoid dyeing the inherently flame resistant fibers when blended with flame resistant cellulosic fibers. As an alternative, these producers suggest using producer colored inherently flame resistant fiber where a colored, flame resistant cellulosic blend is desired. In producer coloring (also known as "solution dyeing"), pigment or other coloring is typically injected into the polymer solution before the fiber is formed. Although providing for adequate colorization of these fibers, producer coloring presents several disadvantages. First, producer colored fibers usually are more expensive than non-producer colored fibers. Second, due to the increased difficulty and cost associated with the production of these fibers, typically only a limited variety of producer colored fibers are available.

In addition to increasing the difficulty of dyeing the inherently flame resistant fibers, dyeing at temperatures below 100° C renders the inherently flame resistant fibers susceptible to substantial laundry shrinkage. Accordingly, where the inherently flame resistant fibers are to be dyed, the dyer is typically left with a choice between acceptable color and shrinkage control but unacceptable flame resistance on one hand (when dyeing above 100°C), and preserved flame resistance but high laundering shrinkage and poor color yield on the other (when dying below 100° C). Notably, the same shrinkage

susceptibility exists in situations where the inherently flame resistant and/or flame resistant cellulosic fibers are not dyed.

From the above discussion, it can be appreciated that it would be desirable to have fabric blends comprising inherently flame resistant fibers and flame resistant cellulosic fibers that avoid the aforementioned problems.

SUMMARY OF THE INVENTION

The present disclosure relates to flame resistant fabrics that comprise a plurality of inherently flame resistant fibers and a plurality of cellulosic fibers containing a flame retardant compound. Normally, the flame resistant fibers were uncrystalized in fiber form and the cellulosic fibers contained a flame retardant compound in fiber form.

In one arrangement, the inherently flame resistant fibers comprise a material selected from the group consisting of aromatic polyamide, polyamide imide, polyimide, and mixtures thereof, while the cellulosic fibers comprise a material selected from the group consisting of rayon, acetate, triacetate, lyocell, and mixtures thereof.

In another arrangement, the fabric contains a residual amount of a dye-assistant selected from the group consisting of N-cyclohexylpyrrolidone, benzyl alcohol, N,N-dibutylformamide, N,N-diethylbenzamide, hexadecyltrimethyl ammonium salt, N,N-dimethylbenzamide, N,N-diethyl-m-toluamide, N-octylpyrrolidone, aryl ether, an approximately 50/50 blend of N,N-dimethylcaprylamide and N,N-dimethylcapramide, and mixtures thereof.

In a further arrangement, the fabric contains a phosphorus compound flame retardant in a concentration of at least approximately 1.4% phosphorus by weight of cellulosic fiber component.

In yet another arrangement, the fabric exhibits a duration of afterflame no greater than 2.0 seconds when subjected to a vertical flammability test conducted in accordance with FTMS 191A Method 5903.1 using a three second exposure.

In a further arrangement, the fabric exhibits a shrinkage percentage of no greater than approximately 7% after 20 launderings conducted in accordance with AATCC Test Method 135-1992, Table I (3)(V)(A)(iii).

The features and advantages of the invention will become apparent upon reading the following specification, when taken in conjunction with the accompanying drawings.

DETAILED DESCRIPTION OF THE INVENTION

As summarized above, the present invention provides fabric blends of inherently flame resistant fibers and flame resistant cellulosic fibers that contain a flame retardant compound. Although not required, the inherently flame resistant fibers, the flame resistant cellulosic fibers, or both typically are dyed through an exhaust process. Where the blend is dyed, the inherently flame resistant fibers of the fabric can be dyed a full shade of color without significantly depleting the amount of flame retardant compound contained in the cellulosic fibers to preserve the flame resistance of the fabric after the dyeing process is completed and through subsequent laundering. It is to be noted that, for the purposes of this disclosure, the term full shade denotes penetration of the subject fiber with dye and fixation of the dye therein, as opposed to mere superficial staining of the

fibers. Irrespective of whether the blends are dyed, shrinkage of the inherently flame resistant fibers is reduced such that the overall fabric shrinkage is within levels considered acceptable by industry standards.

Although the inherently flame resistant fibers can be composed of any material that is inherently flame resistant, it is preferred that these fibers are composed essentially of an aromatic polyamide, polyamide imide, or polyimide, each of which is considered difficult to dye. Most preferably, these fibers will be composed essentially of an aromatic polyamide. Aromatic polyamides are formed by reactions of aromatic diacid chlorides with aromatic diamines to produce amide linkages in an amide solvent. Fibers made of aromatic polyamides are generally referred to by the generic term aramid fiber. Aramid fibers are typically available in two distinct compositions, namely meta-type fibers composed of poly(m-phenylene isophthalamide) commonly referred to as meta-aramid fibers, and para-type fibers composed of poly(p-phenyleneterephthalamide) which are commonly referred to as para-aramid fibers. Meta-aramid fibers are currently available from DuPont of Wilmington, Delaware in several forms under the trademark NOMEX®. For example, NOMEX T-450® is 100% meta-aramid; NOMEX T-455® is a blend of 95% NOMEX® and 5% KEVLAR® (para-aramid); and NOMEX IIIA® (also known as NOMEX T-462®) is 93% NOMEX®, 5% KEVLAR®, and 2% carbon core nylon. In addition, meta-aramid fibers are available under the trademarks CONEX® and APYEIL® which are produced by Teijin and Unitika, respectively. Para-aramid fibers are currently available under the trademarks KEVLAR®, TECHNORA®, and TWARON® from DuPont, Teijin, and Akzo respectively. In accordance with the above description, it is to be noted that, in the present disclosure, when a material name is followed by the term

"fiber," the fiber described is not limited to fibers composed exclusively of the named material.

Meta-aramid and para-aramid fibers share similar characteristics. For instance, both have limiting oxygen indexes (LOI's) approximately between 24 and 30 percent. However, there are significant differences between the two compositions. Notably, para-aramid fibers are considerably stronger than meta-aramid fibers, having tenacity values approximately between 21-27 g/d and a tensile strength of about 400 psi. This strength makes para-aramid fibers particularly useful in law enforcement and military applications. Another significant distinction between meta-aramid and para-aramid fibers is that, although both are difficult to dye, meta-aramid fibers appear to more readily accept dye during the dyeing procedure. Despite being easier to dye, meta-aramid fibers have a greater tendency to shrink when subjected to laundering than do para-aramid fibers. Accordingly, dyed meta-aramid blends must be produced in a manner which additionally prevents or inhibits subsequent shrinking due to laundering.

Another group of fibers that have flame resistant properties and that are difficult to dye are polyamide imides. Sometimes referred to as an aromatic polyamide, polyamide imide is a high performance thermoplastic that is the condensation polymer of trimellitic anhydride and various diamines. Polyamide imide fibers are currently available under the trademark KERMEL® which is produced by Rhône-Poulenc.

A further group of fibers that have flame resistant properties and that are difficult to dye are polyimides. Polyimide is chemically known as poly (4.4'-diphenylmethane-co-tolylenebenzophenonetetracarboxylicimide) and is made by the reaction of benzophenone tetra carboxylic anhydride with a mixture of tolylene and diphenylmethane diisocyanates

in a polar aprotic solvent such as dimethyl-formamide or acetamide. Polyimide fibers are currently available from Lenzing under the trademark P-84®.

Irrespective of the type of inherently flame resistant fibers used, the inherently flame resistant fibers normally are uncrystalized in fiber form prior to dyeing or other processing. As known in the art, "crystalinity" refers to the formation of highly-ordered substances, *i.e.,* crystals, within the fiber. In such crystals, the atoms of the fiber material are ordered in regular chain structures which are packed into an ordered, regular three-dimensional crystal lattice. Generally speaking, crystallized fibers do not readily accept dye. Therefore, dyeing is usually carried out only on uncrystalized fibers. These fibers normally are crystallized, however, by the high temperatures conventionally used to dye such fibers. This crystallization is helpful both in dye retention and in resistance to shrinkage.

In the present invention, one or more of the above identified inherently flame resistant fibers is blended with one or more types of cellulosic fiber. Preferred for the choice of cellulosic fibers are rayon, acetate, triacetate, and lyocell. These cellulosics, although softer and less expensive than the inherently flame resistant fibers, are not naturally resistant to flame. To increase the flame resistance of these fibers, they typically are treated in fiber form with one or more flame retardants such as phosphorus compounds like SANDOLAST 9000®, currently available from Clarion, antimony compounds, and the like. Generally speaking, cellulosic fibers which contain one or more flame retardants are given the designation "FR". Accordingly, the preferred flame resistant cellulosic fibers are FR rayon, FR acetate, FR triacetate, and FR lyocell.

Of the many blends conceivable with the above described listing of preferred fibers, most preferred is a blend of NOMEX IIIA® and FR rayon having a percentage composition of NOMEX IIIA® of at least 20% and a percentage composition of FR rayon of at least 10%. Typically, the fabric will comprise a 50/50, 65/35, or a 35/65 blend of NOMEX IIIA® and FR rayon.

The fabric of the present invention can be dyed and/or shrinkage controlled using customary dyeing equipment. Typically, a dye, a dye-assistant, and a flame retardant for the inherently flame resistant fibers, are combined to form a mixture, (e.g., a dyebath, solution, dispersion, or the like). Although the term "dye-assistant" is used herein, it is to be understood that this material is used even where the inherently flame resistant and/or flame resistant cellulosic fibers are not to be dyed. The fabric is then contacted with this mixture, typically by immersion, and the mixture heated. In accordance with the present invention, a fibrous textile material, *e.g.*, fiber, web, yarn, thread, sliver, woven fabric, knitted fabric, non-woven fabric, or the like, is placed in the bath with the additives using conventional equipment such as dye jets or other appropriate equipment.

The preferred dye-assistants of the present invention are selected from the group consisting of N-cyclohexylpyrrolidone, benzyl alcohol, N,N-dibutylformamide, N,N-diethylbenzamide, hexadecyltrimethyl ammonium salt, N,N-dimethylbenzamide, N,N-diethyl-m-toluamide, N-octylpyrrolidone, aryl ether, Halcomid M-8/10 (an approximately 50/50 blend of N,N-dimethylcaprylamide and N,N-dimethylcapramide), and mixtures thereof. Where the highest degree of shrinkage prevention is desired, the dye-assistant most preferably is selected from the group consisting of N-cyclohexylpyrrolidone, benzyl alcohol, N,N-dibutylformamide, and mixtures thereof.

As an alternative to adding dye-assistant to the bath, the dye-assistant can instead be imbibed into the fibers themselves during production. Exemplary of the types of fibers that could be used in this manner are those disclosed by Vance *et al.* in U.S. Patent No. 4,688,234, and Hodge *et al.* in U.S. Patent No. 5,074,889, both of which are hereby incorporated by reference. As disclosed by Vance *et al.*, typically a surfactant such as hexadecyltrimethylammonium salt or isopropylammonium dodecylbenzenesulfonate is added to the fiber at a level of approximately 5% to 15% by weight. When the fibers are imbibed with dye-assistant, dyeing is conducted in the same manner as described above except that no additional dye-assistant need be added to the dyebath.

In addition to the dye-assistants, a flame retardant compound can also be included in the dyebath, applied as an after dyeing surface treatment, or otherwise incorporated in the fiber to enhance flame resistance or to counteract any deleterious effects of the dye-assistant contained within the inherently flame resistant fibers. Preferred flame retardants are ANTIBLAZE 80® ("AB80®") and ANTIBLAZE 100® ("AB100®") which are both currently available from Albright & Rhodia.

Dyes that can be used advantageously with the present carriers for the dyeing of the inherently flame resistant fibers can include anionic, cationic, disperse dyes, and mixtures thereof. Of these dyes, particularly preferred are cationic dyes. With regard to the dyeing of the cellulosic fibers, preferred are direct, reactive, vat, and sulfur.

As described above, dyeing blends of inherently flame resistant fibers and flame resistant cellulosic fibers has, heretofore, been inadvisable because the dyeing conditions normally used adversely affect one or both types of the fibers. In particular, the high temperatures conventionally deemed necessary to attain adequate dyeing and shrinkage

control of the inherently flame resistant fibers deplete the flame retardant contained in the cellulosic fibers. Notably, this depletion generally is not remedied by the inclusion of additional flame retardant in the dyebath under conventional conditions. Furthermore, these conventional dyeing conditions cause increased subsequent depletion of flame retardant when the fabric blends are laundered. Under the method of the instant invention, however, effective dyeing of the inherently flame resistant fibers can be attained at temperatures below approximately 100° C, without a substantial loss of cellulosic flame retardant and without losing shrinkage control. Notably, shrinkage control can be provided even where the inherently flame resistant fibers are not dyed. Typically, temperatures approximately between 70° C and 100° C are used with approximately 85° C being most preferred. It will be appreciated, however from the data provided below, that temperatures as low as 60° C and even 50° C can be used to dye the blends. However, in that the dyeing process is less efficient and shrinkage prevention more difficult at these lower temperatures, usually temperatures between the stated 70° C - 100° C range are used.

To conduct dyeing and/or shrinkage control of the inherently flame resistant fibers of the blends, a dye-assistant, other additives *e.g.*, a dye) if desired, are preferably applied to the fibers of the fabric using a one-step batch-type process, although split treatment with dye-assistants applied separately from dye is feasible, and in some applications might be desirable. Typically, a roll of fabric is loaded into a jet dyer such as a pressure jet dyeing vessel in which the fabric can be circulated through a apertured venturi contained within the vessel. Once loaded into the vessel, the ends of the fabric are sewn together to form a continuous loop. The fabric can optionally be scoured if desired by

passing it through an aqueous solution that passes through the apertures in the venturi and impinges the fabric. After scouring has been completed, the jet is again charged with water, the selected dye-assistant, dye (if the fabric is to be dyed), and any other auxiliary additives that are desired. Alternatively, where dye-assistant has been imbibed into the fibers, no additional dye-assistant is added to the bath since an adequate amount of dye-assistant is typically already contained within the fibers themselves. In such circumstances, the same steps apply with the exception of the step of adding dye-assistant to the bath.

The temperature of the bath is gradually increased from room temperature to a peak temperature approximately between 70° C and 100° C. Upon reaching the predetermined peak temperature, the bath is maintained at this peak temperature for about 30 to 90 minutes to allow any dye present to fully penetrate the fibers, and to crystallize the fibers. Although the temperatures used are much lower than those normally relied upon for crystallization, acceptable crystallization is achieved through use of the preferred dye-assistants identified herein. It will be appreciated that since the temperature does not reach 100° C, there is no need to increase the pressure of the dyebath beyond atmospheric pressure to prevent boiling. Therefore, all processing can be conducted at constant ambient atmospheric pressure, although a closed vessel and increased pressure may be used to reduce foaming or control odors.

After the expiration of approximately between 30 to 90 minutes at the peak temperature, the bath is cooled until the fabric has reached a temperature at which it can be handled. At this time, the dyebath is discarded and the fabric is again scoured to remove excess dye-assistant or other chemicals contained in the inherently flame resistant

fibers. After all processing has been completed, the fabric then can be finished in the conventional manner. This finishing process can include the application of wicking agents, water repellents, stiffening agents, softeners, and the like. At this stage, the finished fabric normally contains residual dye-assistant in a concentration of approximately 0.5% to 10% owf, depending on the dye-assistant used and total processing. Typically, it is preferred to keep the levels of residual dye-assistants in the lower portion of the range, approximately between 0.5% and 5.0% owf.

Illustrative of the beneficial results attainable when processing at low temperatures as compared with dyeing at high temperatures, Table I provides phosphorous compound retention data for identical samples of a 75/25 blend of NOMEX T-462® and FR rayon that were separately dyed at 250° F (~121° C) and 185° F (85° C). As evidenced by these test data, much larger amounts of phosphorus compound are retained when processing at 185° F as opposed to 250° F, especially after repeated industrial launderings conducted in accordance with NFPA 1975, 1994 ed., s. 4-2.4 as described in the publication entitled <u>Standard of Station/Work Uniforms for Fire Fighters</u>, 1994 edition, which is hereby incorporated by reference.

TABLE I: PHOSPHORUS RETENTION

Dye-Assistant	Peak Dye Temperature	Phosphorus Concentration* After Launderings				
		0	25	50	75	100
benzyl alcohol	250° F (~121° C)	0.66	0.59	0.51	0.35	0.36
aryl ether	250° F (~121° C)	0.54	0.47	0.29	0.44	0.25
none (water)	250° F (~121° C)	0.76	0.63	0.52	0.43	0.34
aryl ether	185° F (85° C)	0.77	0.70	0.64	0.65	0.61
N-cyclohexylpyrrolidone	185° F (85° C)	0.74	0.66	0.65	0.62	0.61
none (water)	185° F (85° C)	0.77	0.70	0.70	0.67	0.67

*Phosphorus concentration was determined by inductively coupled plasma - atomic mission spectroscopy hydrochloric acid digestion of samples.

As shown in Table II, phosphorus retention is maintained when dyeing according to the present invention even at temperatures approaching 100° C. In group A, identical samples of a 65/35 T-462® blend of NOMEX and FR rayon were union dyed at 210° F (~99° C) for 60 minutes using N-cyclohexylpyrrolidone as a dye-assistant. In group B, the samples were union dyed under the same conditions but for 90 minutes at a peak temperature of 210° F. In samples 1-4 of each group, 3g/l of AB80® were added to the dyebath. All samples were also laundered 100 times in accordance with NFPA 1975, 1994 ed., s. 4-2.4. As is evident from these data, phosphorous concentrations stayed above 0.5% when dyed for either 60 or 90 minutes regardless of whether AB80® was added to the dyebath or not.

TABLE II: PHOSPHORUS RETENTION
(Peak Dyeing Temp. = 210° F (~99° C))

Group A: 60 min. peak dye time

Sample No.	Amt. of Dye-Assistant Used (g/l)	Phosphorus Concentration (%)
1	30	0.82
2	35	0.82
3	40	0.74
4	45	0.81
5	30	0.55
6	35	0.58
7	40	0.55
8	45	0.54

Group B: 90 min. peak dye time

Sample No.	Amt. of Dye-Assistant Used (g/l)	Phosphorus Concentration (%)
1	30	0.77
2	35	0.80
3	40	0.84
4	45	0.78
5	30	0.65
6	35	0.68
7	40	0.60
8	45	0.60

Testing has shown that blends of inherently flame resistant fibers and flame resistant cellulosic fibers normally have a phosphorus concentration of at least approximately 0.5% owf to remain adequately flame resistant in accordance with FTMS 191A Method 5903.1 as described in the publication entitled FTMS Textile Test Methods, 1978 edition, which is hereby incorporated by reference. According to Method 5903.1, a three inch by twelve inch fabric specimen is placed in a holder and is suspended vertically over a 1½ inch high methane gas flame. During the test, the material is placed in contact with the flame at the flame's mid-point for a period of twelve seconds. After expiration of the twelve seconds, the flame is extinguished and the material observed to, *inter alia*, determine how long it will continue to burn. This duration of burning after

extinguishment of the methane flame is referred to as "afterflame." Presently deemed acceptable under military and NFPA standards are afterflame durations of 2.0 seconds and less.

Tables III and IV provided below illustrate the criticality of the 0.5% owf measure of phosphorus retention on afterflame control. The data in Table III was obtained by dyeing identical samples of 75/25 blends of NOMEX® and FR rayon with the various listed dye-assistants at 250° F (note that "CHP" stands for N-cyclohexylpyrrolidone and "BPP" stands for emulsified butyl/propylphthalimide). After dyeing, the samples were industrially laundered 0, 25, 75, or 100 times in accordance with NFPA 1975, 1994 ed., s. 4-2.4, and then exposed to flame in accordance with test method FTSM 5903.1 for three seconds instead of twelve. Although only providing a three second exposure to flame, it is believed that the three second flame exposure is a more critical indicator of fabric performance than the twelve second exposure of FTMS 5903.1. In particular, the twelve second duration provides greater opportunity of flame extinguishment (see Table IV). Additionally, the twelve second flame exposure period does not reflect the fabric's resistance to flash fires which typically inflict damage primarily within the first three to four seconds. Under the three second exposure test, afterflames greater than 0.8 seconds provide cause for concern in that afterflames that exceed 0.8 seconds indicate an increased likelihood of injury to the fabric wearer. As is evident from the data of Table II, afterflames greater than 0.8 seconds are consistently avoided when the phosphorus concentrations of the fabric is at least approximately 0.5% owf.

TABLE III: AFTERFLAME RELATIVE TO PHOSPHORUS RETENTION (Three Second Exposure)

Dye-Assistant	No. of Launderings	Phosphorus Concentration (%)	Afterflame (sec)
none (water)	0	0.76	0.1
aryl ether	0	0.54	0.8
acetophenone	0	0.59	0.5
CHP	0	0.69	0.5
benzyl alcohol	0	0.66	0.4
BPP	0	0.78	0.4
none (water)	25	0.63	0.4
aryl ether	25	0.47	0.5
acetophenone	25	0.42	0.4
CHP	25	0.49	0.5
benzyl alcohol	25	0.59	0.4
BPP	25	0.35	0.4
none (water)	50	0.52	0.4
aryl ether	50	0.29	3.5
acetophenone	50	0.35	0.6
CHP	50	0.38	0.6
benzyl alcohol	50	0.51	0.4
BPP	50	0.42	1.1
none (water)	75	0.43	0.6
aryl ether	75	0.44	0.6
acetophenone	75	0.30	29.8
CHP	75	0.39	0.6
benzyl alcohol	75	0.35	1.0
BPP	75	0.44	0.9
none (water)	100	0.34	0.7
aryl ether	100	0.25	4.0
acetophenone	100	0.25	24.1
CHP	100	0.37	1.1
benzyl alcohol	100	0.36	0.8
BPP	100	0.30	2.6

Table IV provides afterflame data of the same fabric and dye-assistants tested in Table III, but after twelve seconds of exposure to flame in accordance with FTMS 5903.1.

TABLE IV: AFTERFLAME RELATIVE TO PHOSPHORUS RETENTION (Twelve Second Exposure)

Dye-Assistant	No. of Launderings	Phosphorus Concentration (%)	Afterflame (sec)
none (water)	0	0.76	N/A
aryl ether	0	0.54	0.0
acetophenone	0	0.59	0.0
CHP	0	0.69	0.0
benzyl alcohol	0	0.68	0.0
BPP	0	0.78	0.0
none (water)	25	0.63	0.0
aryl ether	25	0.47	0.2
acetophenone	25	0.42	0.0
CHP	25	0.49	0.0
benzyl alcohol	25	0.59	0.0
BPP	25	0.35	0.0
none (water)	50	0.52	0.0
aryl ether	50	0.29	0.0
acetophenone	50	0.35	0.0
CHP	50	0.38	0.0
benzyl alcohol	50	0.51	0.0
BPP	50	0.42	0.0
none (water)	75	0.43	0.0
aryl ether	75	0.44	0.0
acetophenone	75	0.30	16.1
CHP	75	0.39	0.0
benzyl alcohol	75	0.35	0.0
BPP	75	0.44	0.0
none (water)	100	0.34	0.0
aryl ether	100	0.25	0.0
acetophenone	100	0.25	13.9
CHP	100	0.37	0.0
benzyl alcohol	100	0.36	0.0
BPP	100	0.30	0.0

Taking into account fabric composition, it has been determined that a phosphorus compound concentration of approximately 0.5% owf translates into a phosphorus concentration of at least approximately 1.4% phosphorus by weight of cellulosic fiber component. In that it is desired to have a fabric which is adequately flame resistant even

after extensive laundering, where phosphorus compound is used as the flame retardant contained in the cellulosic fibers it is preferred that the resultant blends have a phosphorus concentration of at least approximately 1.4% phosphorus by weight of cellulosic fiber component after 100 launderings conducted in accordance with NFPA 1975, 1994 ed., s. 4-2.4.

The dye-assistant used must promote dyeing and/or control shrinkage of the inherently flame resistant fibers at relatively low temperatures. With regard to dyeing, testing was conducted with NOMEX®/FR rayon blends at low temperature to determine the degree of shade depth attainable when dyeing with a variety of alternative dye-assistants. Using several identical samples of a 65/35 blend of NOMEX IIIA® and FR rayon fibers and a laboratory launderometer dye apparatus, ten separate dyeing trials were made, each with a different dye-assistant (see Table V). In each trial, the launderometer tube was loaded at a 10:1 liquor ratio with the dyebath containing 2.8% basic blue dye C.I. #41 owf and 40 g/l of the particular dye-assistant being tested (water was used as a control in the last trial). Dyeing was conducted at 85° C for 60 minutes. Shade depth was measured terms of the lightness or L value of the standardized L,a,b scale. In accordance to this scale, the smaller the value of the L parameter, the deeper the shade, and therefore the greater the extent of dyeing achieved. As indicated in Table V, each of N-cyclohexylpyrrolidone, benzyl alcohol, N,N-dibutylformamide, N,N-diethyl-m-toluamide, aryl ether, N-octylpyrrolidone, and N,N-dimethylbenzamide provided a deep shade of dyeing.

TABLE V: SHADE DEPTH (Peak Dyeing Temp. = 85° C)

Dye-Assistant	Shade Depth (L)
N-cyclohexylpyrrolidone	27.84
N,N-diethyl-m-toluamide	28.30
*aryl ether	27.93
N-octylpyrrolidone	27.80
N,N-dibutylformamide	28.22
butylbenzesulfonamide	36.20
benzyl alcohol	26.98
N,N-dimethylbenzamide	29.06
sodium xylene sulfonate	36.75
water	33.85

*Aryl ether dye-assistants are commercially available from Miles, Hickson Dan Chem, or Stockhausen as proprietary products.

As identified above, acceptable dyeing can be achieved with temperatures below 85° C. Tables VI, VII, and VIII illustrate the depths of shade attainable with dyeing at 50° C, 60° C, and 70° C, respectively. In each trial, identical samples of 100% NOMEX IIIA® were dyed no more than 40 g/l of the selected dye-assistant present.

TABLE VI: SHADE DEPTH (Peak Dyeing Temp. = 50° C)

Dye-Assistant	Shade Depth (L)
N-cyclohexylpyrrolidone	41.55
benzyl alcohol	29.38
N,N-dibutylformamide	40.92
N,N-diethyl-m-toluamide	39.04
N,N-diethylbenzamide	38.20
acetophenone	39.89

TABLE VII: SHADE DEPTH (Peak Dyeing Temp. = 60° C)

Dye-Assistant	Shade Depth (L)
N-cyclohexylpyrrolidone	34.68
benzyl alcohol	27.80
N,N-dibutylformamide	35.84
N,N-diethyl-m-toluamide	38.69
N,N-diethylbenzamide	33.83
acetophenone	31.32

TABLE VIII: SHADE DEPTH (Peak Dyeing Temp. = 70° C)

Dye-Assistant	Shade Depth (L)
N-cyclohexylpyrrolidone	22.62
benzyl alcohol	20.35
N,N-dibutylformamide	25.42
N,N-diethyl-m-toluamide	33.45
N,N-diethylbenzamide	23.42
acetophenone	21.09

In addition to permitting deep coloration of the inherently flame resistant fibers, the method of the present invention reduces the shrinkage of the inherently flame resistant fibers and therefore fabric blends containing such fibers. Table IX provides shrinkage data for 65/35 blends of NOMEX IIIA® and FR rayon fibers dyed with 40 g/l of various carriers at 85°C for 60 minutes. Each fabric sample was then subjected to 5, 10, and 20 AATCC Test Method 135-1992, Table I (3)(V)(A)(iii) launderings as described in the publication entitled American Association of Textile Chemists and Colorists, 1992 edition, which is hereby incorporated by reference. As is evident from Table IX, the least amount of shrinkage occurred when the dye-assistant used was N-cyclohexylpyrrolidone, benzyl alcohol, and N,N-dibutylformamide, with the warp direction of the fabric only shrinking 3.8%, 5.7%, and 6.6% after 20 launderings.

TABLE IX: FABRIC SHRINKAGE (Peak Dyeing Temp. = 85° C)

	Fill Shrinkage (%)			Warp Shrinkage (%)		
Dye-Assistant	5x	10x	20x	5x	10x	20x
N-cyclohexylpyrrolidone	1.5	2.1	2.1	3.0	3.5	3.8
N,N-diethyl-m-toluamide	4.1	6.1	7.1	5.1	7.8	9.7
aryl ether	4.6	7.1	10.2	5.1	9.1	12.6
N,N-octylpyrrolidone	4.1	5.6	7.7	5.1	7.5	10.2
N,N-dibutylformamide	2.1	3.1	3.1	3.0	4.9	5.7
Butylbenzesulfonamide	6.2	7.7	11.8	7.5	11.2	18.7
benzyl alcohol	1.0	3.1	4.7	2.7	4.9	6.6
N,N-dimethylbenzamide	4.1	7.1	9.6	6.5	9.7	12.4
sodium xylene sulfonate	5.6	8.6	12.7	7.4	11.9	16.1
Water	5.6	8.2	12.2	7.2	11.7	15.9

Table X provides shrinkage data for identical samples of 100% NOMEX IIIA® fabric at 70°C for 60 minutes. Afterbeing dyed, each sample was laundered 5, 10, and 20 times in accordance with AATCC Test Method 135-1992, Table I(3)(V)(A)(iii). As shown in this table, significant shrinkage control is obtainable at temperatures as low as 70°C.

TABLE X: FABRIC SHRINKAGE (Peak Dyeing Temp. = 70° C)

	Fill Shrinkage (%)			Warp Shrinkage (%)		
Dye-Assistant	5x	10x	20x	5x	10x	20x
N-cyclohexylpyrrolidone (30 g/l)	3.4	5.2	8.2	5.9	7.3	11.4
N-cyclohexylpyrrolidone (40 g/l)	4.1	5.2	9.3	5.2	7.5	12.4
benzyl alcohol (30 g/l)	3.3	4.9	8.0	4.9	6.7	11.1
benzyl alcohol (40 g/l)	4.1	5.2	8.2	4.1	6.4	10.3
N,N-dibutylformamide (40 g/l)	5.7	7.7	12.9	7.2	10.1	16.0

Although the shrinkage data provided above in Tables IX and X pertain specifically to shrinkage after dyeing the inherently flame resistant fibers, it is to be noted that the shrinkage of the inherently flame resistant fibers of these fabric blends can be controlled without actually dyeing the fibers. For instance, if a blend having just the cellulosic fibers dyed (or no fibers dyed) were desired, the dyeing process described above would be followed with the exception that dye for the inherently flame resistant fibers would not be included in the bath or other medium. Similarly, just the inherently flame resistant fibers of the blend could be dyed according to the present method, if desired.

The results of Tables I-X illustrate that blends of inherently flame resistant fibers such as aromatic polyamides, polyamide imides, and polyimides, and cellulosic fibers such as rayon, acetate, triacetate, and lyocell that contain a flame retardant compound can be effectively dyed such that the inherently flame resistant fibers are dyed a full shade of color (including deep shades, if desired), and the amount of flame retardant compound

contained in the cellulosic fibers substantially maintained such that there is not a significant loss of flame resistance in the end fabric. Moreover, these results show that where inherently flame resistant fibers are susceptible to laundering shrinkage, dyeing and/or shrinkage inhibiting according to the present invention significantly reduces such shrinkage.

In the specification and examples, there have been disclosed preferred embodiments of the invention, although specific terms are employed, they are used in a generic and descriptive sense only and not for the purpose of limitation, the scope of the invention being defined by the following claims.